Frontiers article

The Jones-Ray effect reinterpreted: Surface tension minima of low ionic strength electrolyte solutions are caused by electric field induced water-water correlations

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ABSTRACT

The surface tension of electrolyte solutions exhibits a minimum at millimolar electrolyte concentrations and then rises with increasing concentration. This minimum, known as the Jones-Ray effect, has been hotly debated over the past ~80 years. If not considered as an artifact, it is typically ascribed to a phenomenological rare binding site for ions or ion pairs. Here, we propose an alternative underlying mechanism, namely that the hydrogen bond network of water responds to the collective electrostatic field of ions by increasing its orientational order, supported by recent surface tension measurements of NaCl solutions in H_2O and D_2O, and second harmonic scattering experiments in combination with ion resonant second harmonic reflection experiments. Recent thermodynamic and purely electrostatic treatments of the surface tension provide support for this interpretation. In addition, concerns related to possible artifacts influencing the measurements are quantified experimentally.

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1. Introduction

The surface tension of aqueous salt solutions in contact with air generally increases with salt concentration. This increase in the surface tension was first shown and explained, almost 8 decades ago, by Onsager and Samaras with a model based on Debye-Hückel theory [1]. More specifically, the surface tension increases as a result of ion exclusion from the interface that happens as a consequence of electrostatic image forces [1,2]. This surface tension increase as a function of electrolyte concentration is shown in Fig. 1A for a selection of common electrolytes including $BaCl_2$, KI, KCl and NaCl. The data are adapted from Ref. [3]. It can be seen from Fig. 1A that at concentrations > 0.5–1 mol/kg, the surface tension increases linearly. The increase starts in fact already at ~ 50 mM [4]. The slope of the monotonic increase depends on the chemical nature of the electrolyte. This specificity could not be captured by the model of Onsager and Samaras. In recent years, experimental and molecular dynamics simulation studies have shown that there is a specificity in the exclusion of simple ions from the interfaces [5–16]. For instance, ions with high polarizability, i.e., I^-, SCN^-, and Br^-, are less excluded from or even included

into the air/water [15,17]. macromolecule/water [10] or oil/water [8,18] interface. Several models have been proposed to explain this ion specificity [5,12,19–26]. What all these explanations have in common, is that the size, polarizability and molecular interactions such as hydrogen bonding and ion-dipole interactions are the main ingredients of the observed behavior. As such, although there remain some open questions, there is a general agreement as to what causes the increase in surface tension. Curiously, such a consensus is not present for ionic strengths below ~50 mM where surface tension measurements have and still are causing controversy.

First, there is the matter of the experimental data. Just one year after Onsager and Samaras introduced their model of ion repulsion at interfaces, Jones and Ray reported on the surface tension of aqueous KCl solution at very low ionic strength. They measured, using the capillary rise method, that the surface tension gradually decreases reaching a surface tension minimum at ~1 mM. Above 1 mM the surface tension gradually increases again according to the above described trend [27]. Fig. 1B displays the data from Ref. [27] for KCl. In subsequent years, using the same method, the same surface tension trend was reported for a total of 13 different electrolyte solutions [28–31]. Jones and Ray showed that all the tested salts have a surface tension minimum near 1 ± 0.5 mM and that the minimum in their measured response corresponded to a change of ~ −0.18‰, a small but reproducible change. The results

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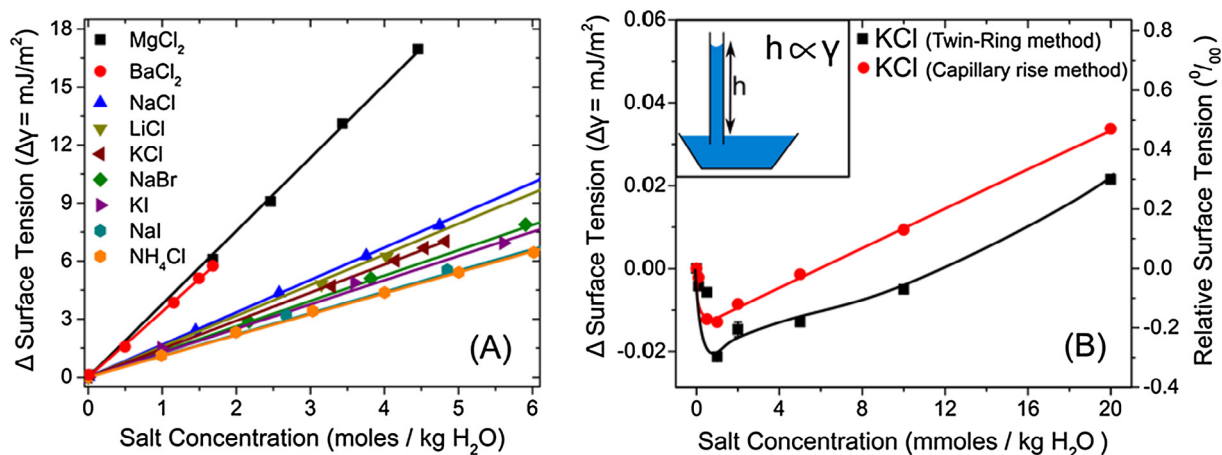   E-mail address: sylvie.roke@epfl.ch (S. Roke).

Fig. 1. Surface tension of electrolyte solution in contact with air. (A) Surface tension values of air/aqueous solution interfaces as a function of concentration for various salts as indicated in the legend (adapted from Ref. [3] with permission and fitted with straight lines). Note that the graph does not report on any data points below an electrolyte concentration of 0.5 mol/kg H_2O. (B) Relative change in the surface tension of KCl solution as obtained from the capillary rise method (red circles) by Jones and Ray [27], along with the surface tension values of KCl (black squares) measured with a twin-ring apparatus by Dole and Swartout (adapted from Ref. [32]). The red and black lines are guides to the eye. The inset shows a schematic of the capillary rise method [41]. In this method, the height of an aqueous solution (h) in a thin capillary is proportional to the surface tension ($h \propto \gamma$). All the 13 tested salts by Jones and Ray yield the same trend as the red data set.

by Jones and Ray have been hotly debated: Some researchers have reproduced their results and have proposed an explanation [13–14,32–34]. Others have questioned the validity of the experiments. Langmuir blamed the minimum on artifacts of the capillary rise method, *viz.* the thickness of the wetted film on the glass walls was not well determined [35,36]. Cassel presented an alternative view that an increase of the wetting angle may be involved [37]. Coolidge suggested that the contact angle may be imaginary [38]. In contrast, Dole and Swartout reproduced the Jones-Ray surface tension data with a differential surface tension apparatus, a so-called twin-ring tensiometer, where double 90% Platinum/10% Iridium alloy rings were utilized to measure the surface tension of salt solutions [32]. Another method for measuring surface tension, the bubble pressure method, was employed to measure changes in surface tension. The surface tension decline could be observed, but only with long-lived bubbles. Short-lived bubbles did not show a decrease in the surface tension. This result again raised validity questions, this time about the impact of organic impurities and the influence of atmospheric $CO_2(g)$ in these experiments [39,40].

A second issue is the matter of the underlying mechanism. Why would the surface tension have a minimum at very low ionic strengths and why is this not ion specific? Dole was the first accepting the validity of the experimental results by Jones and Ray and suggested a mechanism that is based on the adsorption of ions to a phenomenological and exceptional binding site (in his own wording 'active spot') on the water surface [42].

Since surface tension measurements report on free energy changes that are not specific to any of the constituents of the system or to any mechanism, a more surface specific probe is needed. A decade ago, Koelsch and Motschmann performed ellipsometry measurements on salt solutions [43–45]. They quantified their method and calibrated their instrument against surface tension and second harmonic generation (SHG) of ionic dye solutions, and determined that their experiment would be sensitive enough to detect the minute amounts of ions in the interfacial region that are necessary to reduce the surface tension. However, no change in the ellipsometric response was found below 10 mM. (P. Koelsch, private communication 'I thought by that time that we should be able to see ion induced differences in the ellipsometric angle Δ, but it stayed dead flat.') Around the same time, Petersen and Saykally reported ion resonant SHG surface reflection experiments

that showed an increase in the SHG response at concentrations ∼ 0.5 mM and saturating at ∼ 100 mM [13,14]. The resulting intensity change as a function of salt concentration followed the shape of a Langmuir isotherm. It was therefore concluded that ions bind to specific surface sites already at very low salt concentrations. The mechanism for this behavior was essentially identical to that of Dole using the same phenomenological rare binding site argument. After all, at very low ionic strengths ions are preferably solvated, as the hydration free energy of most ions are negative and thus, favorable. Recently, Garde and coworkers suggested that such a rare binding site could involve the pairing of ions with the counterions being situated at the interface [34], even though this should happen at very low ionic strengths where ion pairs have not been observed experimentally. Overall, the Jones-Ray effect has been considered as a surface phenomenon and the suggested mechanisms involve a rare, unknown ion or ion pair binding site. This non-ion specific binding site that saturates around a few mM salt concentration is hard to reconcile with physical arguments and thus many researchers have been, and still are, questioning the Jones-Ray effect and its explanation [13.14,29,31,33.34,37–40].

In this work we revisit a recent reproduction of the Jones-Ray effect [33], measured with the Wilhelmy plate method for NaCl in H_2O and D_2O (Fig. 2A). We first discuss the interpretation of a surface tension measurement using the Wilhelmy plate method and then examine the abovementioned experimental concerns in detail, considering the contact angle, the effect of dissolved $CO_2(g)$ and the influence of organic impurities by means of explicit measurements. We then consider the interpretation starting from thermodynamic expressions and discuss possible mechanisms behind the Jones-Ray effect based on bulk specific and surface specific second harmonic measurements. These measurements show changes for light and heavy water that match the difference observed in the surface tension measurements, and paint a picture of the reorientation of (bulk) water in the extended hydration shells being responsible for the observed decrease in surface tension, rather than filling up of surface binding sites. Thus, instead of the electrolytes being attracted by the interface to a rare binding site, it is the bulk solution that is responsible for the observed effect. We finish with a discussion of two recently published thermodynamic and purely electrostatic treatments of the surface tension that support this interpretation.